

RESEARCH PAPER

Green Approach to Synthesis of Pt and Bimetallic Au@Pt Nanoparticles Using *Carica Papaya* Leaf Extract and Their Characterization

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ABSTRACT

This study reports a green approach to synthesis of monometallic platinum nanoparticles (Pt NPs) and bimetallic aurium@platinum nanoparticles (Au@Pt) using aqueous leaf extract of *Carica papaya* as a reducing and stabilizing agent. The nature and morphology of as-synthesized PtNPs and bimetallic Au@Pt NPs were characterized using UV/vis spectroscopy (UV-vis), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), and energy dispersive X-ray (EDX). HRTEM images reveal that the as-synthesized PtNPs are in the size range of 3.94–5.48 nm with average particle size of 4.50 ± 0.80 . The HRTEM image of as-synthesized Au@Pt shows distinguishable objects of almost same spherical shape but having different contrast with size ranging from 4.17 to 13.23 nm and average particle size of 8.70 ± 2.50 nm. The EDX data of Au@Pt nanoparticles reflects bimetallic nature, and the individual metal of the bimetallic Au@Pt nanoparticles are present almost in the ratio 2:1. The narrow size distribution and small average size (< 10 nm) of the as-synthesized nanoparticles are highly potential in catalytic applications.

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INTRODUCTION

The increasing applications of platinum nanoparticles (PtNPs) in organic catalysis, fuel cells, hydrogen storage, electrocatalysis and bioelectronics are due to their high melting points, good anti-corrosive properties and resistance to chemical attack [1-4]; while the crucial applications of gold nanoparticles (AuNPs) on the other hand are due to their size and shape related electronic and optical properties [5-8]. The versatile physicochemical properties of bimetallic Au@Pt nanostructures coupled with their ability to exhibit synergistic effects on optical, electrical and catalytic properties, which are entirely in contrast

to their monometallic counterparts, have made scientists to develop special interest on them [9]. In the present study, we have demonstrated a suitable green chemistry approach to the synthesis of PtNPs and bimetallic Au@Pt nanostructures using *Carica papaya* leaf extract as reducing and capping agents. The usage of leaf extract from *Carica papaya* plant takes full advantage of unwanted waste material which is economically friendly, efficient and safe; and also provides alternative way of addressing disposal problems associated with these wastes. The mechanism for the bio-reduction process by the bioactive compound of the plant has also been proposed.

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Fig. 1. Photo of *Carica papaya*.

MATERIALS AND METHODS

Collection and extract preparation

Fresh *Carica papaya* leaves (Fig. 1) were collected from our campus, and thoroughly washed with water to remove any particulate matter and later rinsed with distilled water to obtain clean leaves. The clean leaves were allowed to dry for 2–3 days at laboratory temperature and then grind into powdery form. The leaf extract solution was prepared by taking 20 g of powdered leaves in a 250 mL Erlenmeyer flask with 200 mL of deionized water and the mixture was boiled at 80°C for 30 min. The mixture was cooled and vacuum filtered, and the resulting filtrate (extract) was used for further analysis within a week.

Synthesis of nanoparticles

The bimetallic Au@Pt NPs were synthesized as follows: thoroughly mixed 40 mL of 1 mM aqueous HAuCl_4 solution and 40 mL of 1 mM aqueous $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution was prepared. The *C. papaya* leaf extract (20 mL) was then added to this solution with vigorous stirring at 100°C for 5 h, where spontaneous reduction results in the formation of Au@Pt NPs solution. The reduced Au@Pt NPs solution was centrifuged at 3,000 rpm for 30 min in order to disperse the nanoparticles in liquids and later purified by repeated centrifugation at 3,000 rpm for 15 min. The solid Au@Pt NPs were washed with distilled water to remove the impurities and dried at 100°C. For control experiment, the same amount of the mixed aurium and platinum solution was maintained separately under the same reaction conditions. The PtNPs were prepared in the same manner by mixing 80 mL of 1 mM aqueous $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution with 20 mL of *C.*

papaya leaf extract, followed by same purification procedure as described for the bimetallic Au@Pt nanostructures.

Characterization of nanoparticles

The as-synthesized PtNPs and Au@Pt nanoparticles were characterized by UV–visible spectrophotometer on a Shimadzu (Cecil 7200 model). The FTIR spectra measurements of dried PtNPs and Au@Pt NPs in the powdered form were measured using IRAffinity 1S Shimadzu spectrometer in KBr pellets. Size and morphology of the as synthesized PtNPs and Au@Pt NPs were determined by high resolution transmission electron microscope (HRTEM) coupled with Energy dispersive X-ray spectroscopy (EDX) Oxford detector (model X-Max. A JOEL-2100F, USA), at an energy range 0–20 keV.

RESULTS AND DISCUSSION

UV-visible spectroscopy

Fig. 2 shows the UV–visible spectra of the aqueous *C. papaya* leaf extract as well as the PtNPs and Au@Pt NPs obtained by aqueous *C. papaya* leaf extract after reaction periods of 5 h at 100°C. The UV spectrum of the aqueous *C. papaya* leaf extract (Fig. 2a) shows bands at λ_{max} 224 and 227 nm (K-bands). These bands can be due to $\pi \rightarrow \pi^*$ transition of the absorbance of ring related to the electron-donating substituted benzoyl system. Recent studies [10,11] have reported the presence of phytoconstituents in the leaf extract of *C. papaya* to include phenolic compounds, tocopherol, ascorbic acid, flavonoids, and reducing sugars. Therefore, the observed transitions are probably related to these bioactive compounds in the leaf extract, which are responsible for the bioreduction process and formation of PtNPs and Au@Pt NPs via π -electron interactions [12,13]. Hence, the aqueous leaf extract of *C. papaya* acts as a reductant and stabilizer agent.

The surface plasmon resonance (SPR) of PtNPs is found in the ultraviolet range at 211 nm, which unlike other noble metal nanoparticles such as gold and silver that display SPR in the visible range [14], thus indicating the formation of Pt(0). The SPR peak at 211 nm, which is assigned to PtNPs is slightly red-shifted to 220 nm while the usual SPR absorbance of gold (520–560 nm) [15] is completely depressed in the bimetallic nanostructures. Since the SPR wavelength of nanoparticles is size-dependent [15], the red shift of the SPR peak of

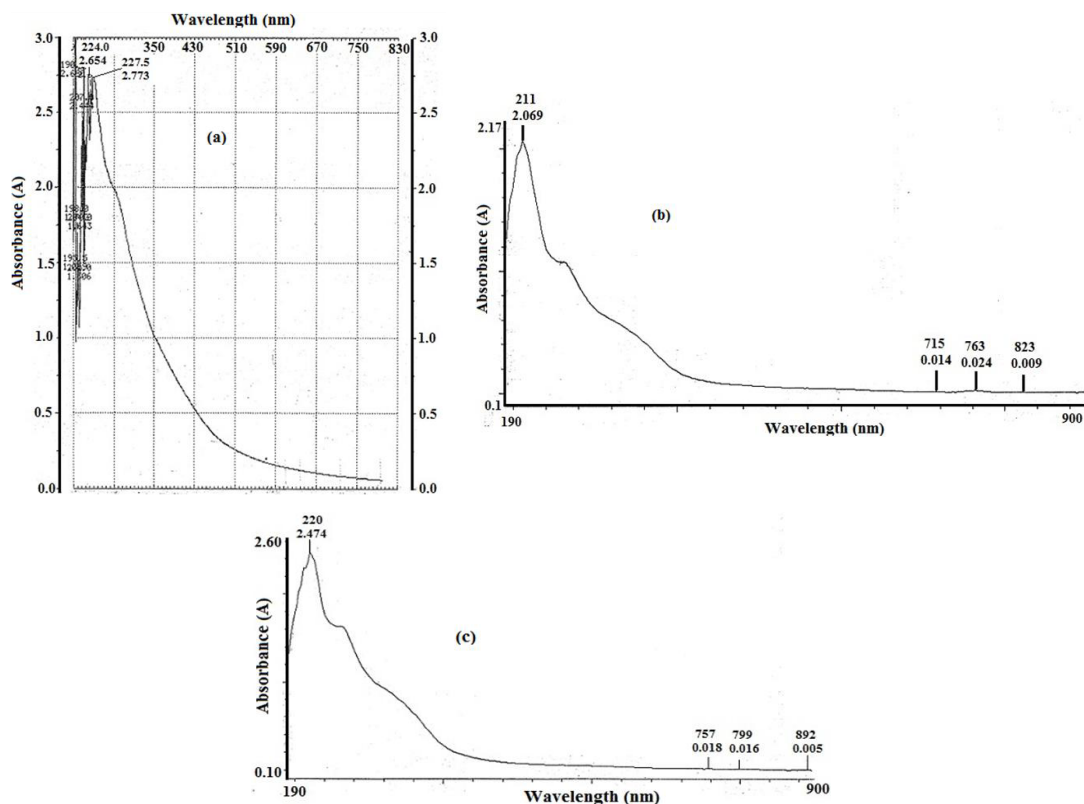


Fig. 2. UV-Vis absorption spectra of *C. papaya* leaf extract (a), PtNPs (b) and Au@Pt NPs (c)

PtNPs in the as-synthesized Au@Pt may indicate the formation of bigger platinum nanoparticles in the bimetallic nanostructures. The peaks at 715, 763 and 823 in the PtNPs (Fig. 2b) were also red-shifted to 757, 799 and 892 nm in the bimetallic Au@Pt (Fig. 2c). The complete disappearance of SPR peak of AuNPs suggests that the bimetallic Au@Pt NPs formed may have a thin non-uniform gold shell surrounded by a thick platinum core [16]. Due to the fact that the gold shell is not thick and dense enough, the SPR peak might have disappeared as a result of effective interaction of the core with the electromagnetic field [17]. Therefore, the disappearance of the SPR peak of gold and the red shifted of the SPR peak in the PtNPs absorption could indicate the formation of Au@Pt NPs with a core/shell or alloy structure rather than phase separate monometallic with two separated SPR peaks of gold and platinum nanoparticles [18-20].

FTIR analysis

FTIR analysis was used to identify the possible biomolecules responsible for the reduction of the

metal precursors and the stabilization of the NPs. The FTIR spectrum of the *C. papaya* leaf extract (Fig. 3a) shows a number of vibration bands for O–H group (3300 cm^{-1}), C=O group or C=C stretch of aromatic compound (1635 cm^{-1}), C≡N group (2391 cm^{-1}), C≡C group (2158 cm^{-1}), C–H bend of aromatic compound (1971 cm^{-1}), and C–O stretch of aromatic ester or C–N stretch of aromatic amine (1301 cm^{-1}). Therefore, we established that some water-soluble polyhydroxy biomolecules in the *C. papaya* leaf extract such as flavonoids and reducing sugar are responsible for the reduction of precursor metal ions.

The formation of PtNPs and Au@Pt nanostructures shows distinctive differences in the shapes and positions of peaks, indicating the interaction between precursor metal ions and the involved functional group of the biomolecules for the production of NPs. The stretching vibration of the O–H group and C–H bend of aromatic compounds were blue shifted in both NPs, indicating the involvement of phenolic hydroxyl group and π - electrons of aromatic compound in the reduction mechanism by donating electrons

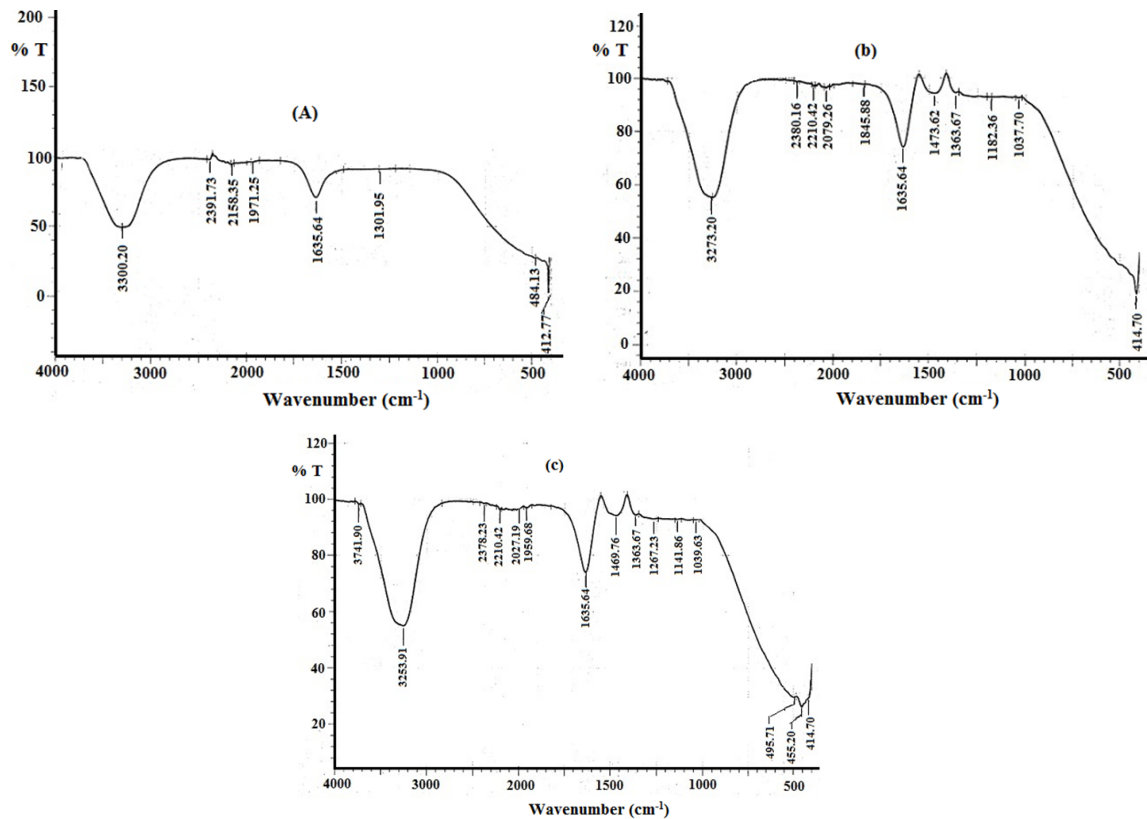


Fig. 3 FTIR spectra of *C. papaya* leaf extract (a), PtNPs (b) and Au@Pt bimetallic NPs (c).

and forming quinone derivatives. A new vibration band for O–H group (3741 cm⁻¹) appeared in spectrum of Au@Pt. Also, the FTIR spectra of both NPs show appearances of more peaks for C≡N, C≡C, C–O and C–N functional groups, indicating the presence of capping ligands with high affinity for coordination (interaction) with metallic ions, and which might have caused the observed blue shift in the absorption bands of the NPs. The possible reaction mechanism of typical polyhydroxyl compound with Pt⁴⁺ ions for example, accepting electrons into their vacant d-orbitals and get converted into Pt⁰ with formation of quinone derivatives is hereby proposed as shown in Fig. 4.

HRTEM and EDX analyses

High resolution-TEM (HRTEM) was used to characterize the lattice arrangement and crystallinity of the NPs. Figure 4 shows the HRTEM images of as synthesized PtNPs and Au@Pt NPs. The NPs exhibit highly uniform morphology, and were well stabilized in the matrix of biomaterial with no sign of agglomeration. The PtNPs have the

particle size range between 3.94 and 5.48 nm with average particle size of 4.50 ± 0.76 nm (Fig. 5a). The HRTEM image of as synthesized Au@Pt shows distinguishable objects of almost same spherical shape but having different contrast with size ranging from 4.17 to 13.23 nm and average particle size of 8.70 ± 2.50 nm (Fig. 5b). So, the objects may be distinguished by the light Pt clusters from the dark gold particles, due to the different scattering power of the two metals.

The elemental composition of the as synthesized NPs was obtained by energy dispersive X-ray analysis (EDX) and is summarized in Table 1. The EDX data confirms the presence of Pt in the PtNPs, which further demonstrates that PtNPs were formed by reduction of the Pt⁴⁺ ions. The EDX data of Au@Pt NPs (Table 1) reflects bimetallic nature, and the individual metal of the bimetallic Au@Pt nanostructures are present almost in the ratio 2:1. The EDX data of as synthesized PtNPs and bimetallic Au@Pt NPs show the presence of other elements like C, N, O and Cu as major elements while other are present as minor elements (Table 1). The Cu

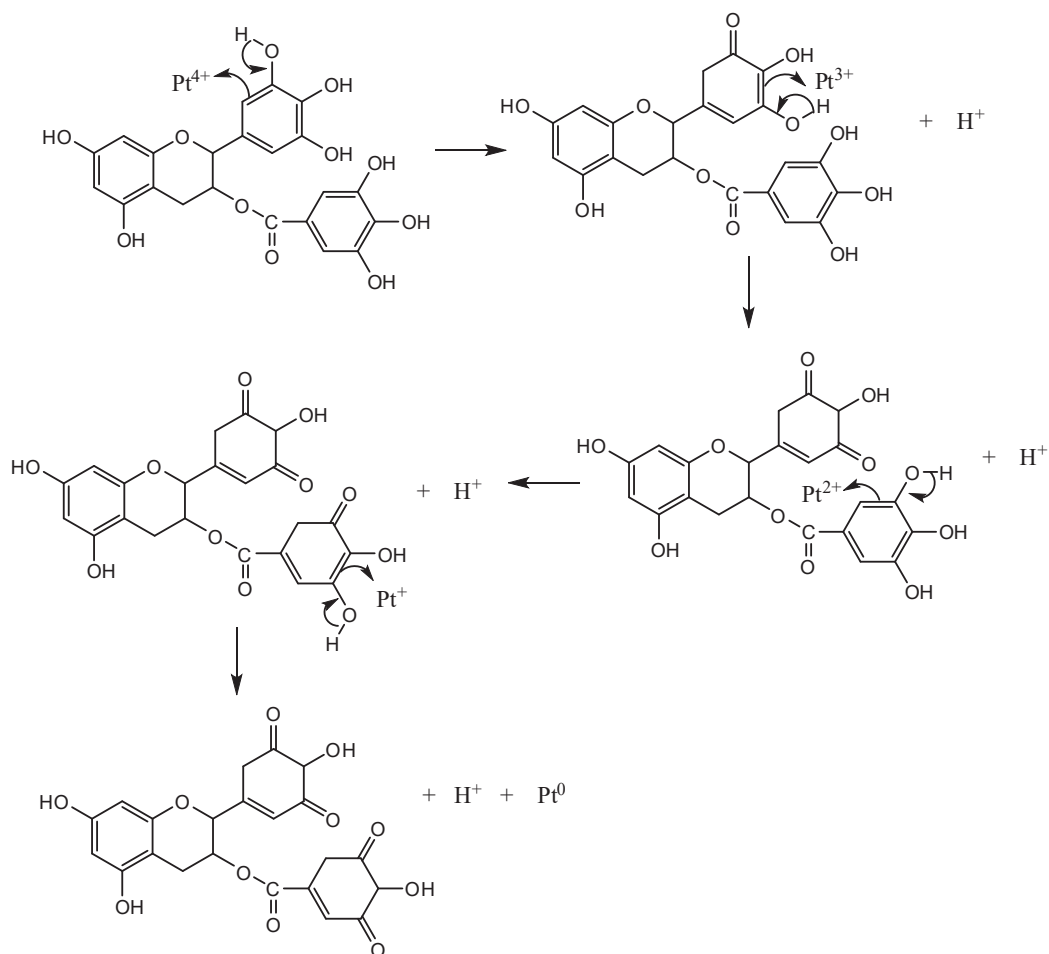


Fig. 4. Proposed mechanism for the bioreduction of Pt^{4+} to Pt atom by a typical polyphenolic compound in *C. papaya*.

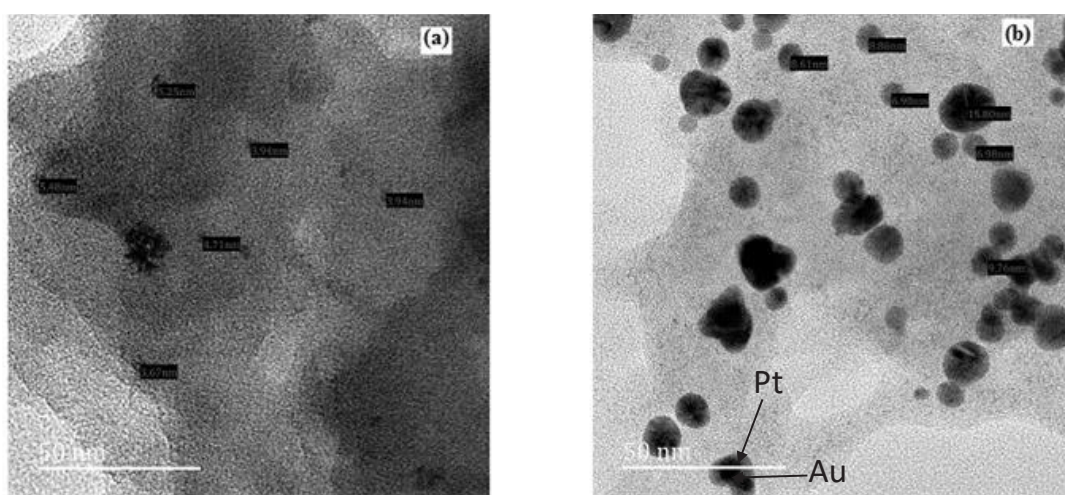


Fig. 5. HRTEM images of PtNPs (a), and Au@Pt NPs (b).

Table 1. EDX results for the as-synthesized PtNPs and Au@Pt NPs using *Carica papaya* leaf extract

Nanoparticles	Element	Weight (%)	Atomic (%)
Pt NPs	C K	57.89	82.77
	N K	3.56	4.36
	O K	5.89	6.32
	Si K	0.23	0.14
	S K	0.61	0.33
	Cl K	0.72	0.35
	Ca K	0.25	0.11
	Cr K	0.35	0.12
	Co K	0.21	0.06
	Cu K	14.85	4.01
	Zn K	0.47	0.12
	Pt L	14.98	1.32
	Total	100.00	
Au@Pt NPs	C K	35.07	72.32
	N K	3.61	6.39
	O K	4.57	7.08
	Mg K	1.88	1.91
	P K	1.59	1.27
	Cl K	0.38	0.27
	K K	0.16	0.10
	Ca K	0.89	0.55
	Cr K	0.44	0.21
	Mn K	0.09	0.04
	Fe K	0.41	0.18
	Co K	0.46	0.19
	Cu K	11.13	4.34
	Zn K	0.70	0.26
	Pt L	11.88	1.51
	Au L	26.74	3.36
Total	100.00		

peak corresponds to the copper grid while C, N, and O peaks originated from biomolecules in leaf extract of *C. papaya* that surround the NPs as capping and stabilizing agents.

CONCLUSION

This study has demonstrated a green approach to the synthesis of Pt and Au@Pt NPs using leaf extract of *C. papaya*. The bioreduction of precursor metal ions is facilitated by polyphenolic compounds in the leaf extract, and is also responsible for stabilization and capping of the NPs. Characterization results show that the Au@Pt NPs were alloyed with individual metals of the bimetallic present almost in the ratio 2:1. These as-synthesized nanoparticles have narrow size distribution and very small average size (< 10 nm), property that could enhance their potential for catalysis.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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